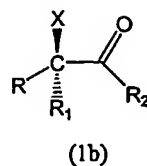
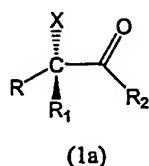
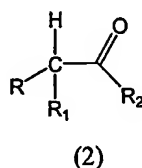


Claims

1. A process for the catalytic asymmetric synthesis of an optically active compound of the formula (1a) or (1b)



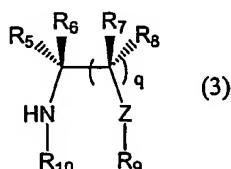
- 5 wherein R is an organic group; X is halogen; R₁ and R₂ which may be the same or different represents H, or an organic group or R₁ and R₂ may be bridged together forming part of a ring system; R and R₂ may be bridged together forming part of a ring system; with the proviso that R and R₁ are different and R₂ when different from H is attached through a carbon-carbon bond, comprising the step of reacting a compound of the formula
- 10 (2)



- 15 with a halogenating agent in the presence of a catalytic amount of a chiral nitrogen containing organic compound.

2. The process according to claim 1 wherein R₂ is H or an optionally substituted C₁₋₁₀ alkyl group or R and R₂ are bridged together forming part of a ring system.
3. The process according to claim 1 or 2 wherein R₁ is H or an optionally substituted C₁₋₁₀ alkyl group.
4. The process according to any of the preceding claims wherein R is an optionally substituted C₁₋₁₀ alkyl group, an optionally substituted C₂₋₈ alkylene group or a C₁₋₃-alkylaryl group.
5. The process according to claim 4 wherein R is an optionally substituted C₁₋₆ alkyl group, an optionally substituted C₂₋₄ alkylene group or a C₁₋₂-alkylaryl group.

6. The process according to claim 4 or 5 wherein R_1 and R_2 are H.
7. The process according to claim 1 wherein the chiral nitrogen containing organic compound is selected among compounds having a primary or secondary nitrogen atom or when appropriate in one of its salt forms.
8. The process according to claim 7 wherein the chiral nitrogen containing organic compound is selected among compounds of the formula (3)



wherein q is 0 or 1;

R_5, R_6, R_7, R_8 , which may be the same or different represents H, alkyl, haloalkyl, alkoxy, OH, amino, amide, silyl, silyl ether, COR_{11} , optionally substituted aryl, an optionally substituted heterocycle, alkyl substituted with at least one OH group, an optionally substituted amino group or optionally substituted aryl or heterocycle or R_5 and R_6 together or R_7 and R_8 together may represent a carbonyl group or when q is 1, R_5 with either R_7 or R_8 may be bridged together forming part of a ring system; R_{11} represents an optionally substituted amino group or OR_{12} wherein R_{12} represents H, alkyl or phenyl;

R_9 and R_{10} , which may the same or different represents H, alkyl, OH, or alkoxy; or R_9 and R_{10} may be bridged together forming part of a ring system;

Z is S, O, $\text{C}=\text{O}$, $\text{C}(\text{R}_{14})_2$, $\text{N}-\text{R}_{14}$ wherein R_{14} is R_5 ;

with the proviso that the groups $R_5, R_6, R_7, R_8, R_9, R_{10}, R_{14}$, and Z are selected so that the compound (3) is a chiral compound.

9. The process according to claim 8 wherein q is 1; R_5, R_6, R_7, R_8 which may the same or different represents H, COR_{11} , optionally substituted aryl or methyl substituted with at least one of the following, an OH group, an optionally substituted amino group or an optionally substituted aryl or heterocycle group; or R_5 and R_7 together represents a C_{3-5}

alkylene bridge;

R₁₁ represents OH, NH₂ or NH-alkyl;

R₉ and R₁₀ are H or R₉ and R₁₀ together represents a methylene bridge optionally substituted with phenyl, benzyl, COOH or CO-alkoxy;

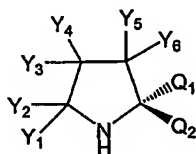
5 Z is CH-R₁₄ or N-R₁₄ wherein R₁₄ represents H or alkyl.

10. The process according to claim 9 wherein either R₅ or R₆ represents H; R₇ and R₈ represents H; R₉ and R₁₀ together represents a methylene bridge and Z is CH₂.

10 11. The process according to claim 3 wherein R₁ is H and R and R₂ each represents an optionally substituted C₁₋₁₀ alkyl group or R₂ together with R forms an optionally substituted C₃₋₅-alkylene bridge optionally with one or more of the carbon atoms being replaced by a heteroatom.

15 12. The process according to claim 1 wherein one or more acids are added to the reaction media.

13. The process according to claim 8, wherein the compound of formula (3) is a compound of formula (4)



(4)

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wherein Y₁, Y₂, Y₃, Y₄, Y₅, Y₆ which may be the same or different represents H, an alkyl, haloalkyl, an aryl, an alkylaryl, a heterocycle, a halogen, a hydroxyl, a carbonyl, an alkoxy, an ester, an amine, an amide, a silyl, a silyl ether, or Y₂ and Y₃ or Y₄ and Y₅ may be bridged together forming part of a ring system one of Q₁ and Q₂ represent H, alkyl, haloalkyl, alkylaryl and the other the group CY₇Y₈(OY₉) wherein Y₇ and Y₈ which may be the same or different represents alkyl, haloalkyl, an alkylaryl, a heterocycle, or optionally substituted aryl and Y₉ represents a silyl group.

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14. A compound of the formula (4) as disclosed in claim 13.

15. The compound according to claim 14, wherein Y₁, Y₂, Y₃, Y₄, Y₅, Y₆ each represents H; one of Q₁ and Q₂ represents H; Y₇ and Y₈ each represents an optionally substituted aryl group, wherein the substituents are selected among alkyl and haloalkyl; Y₉ represents tri-alkyl silyl.

16. The compound according to claim 15, wherein Y₇ and Y₈ each represents 3,5-di-trifluoromethyl phenyl and Y₉ represents trimethyl silyl.

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17. The compound according to claim 15, wherein Y₇ and Y₈ each represents 3,5-di-methyl phenyl and Y₉ represents trimethyl silyl.